



Dye sensitized visible light degradation of phenolic compounds

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ABSTRACT

The present research work reports the eosin Y (EY) and fluorescein (FL) sensitized visible light degradation of phenol, 4-chlorophenol (CP), 2,4-dichlorophenol (DCP) and 2,4,6-trichlorophenol (TCP) using combustion synthesized nano-TiO₂ (CS TiO₂). The rate of degradation of the phenolic compounds was higher in the presence of EY/CS TiO₂ compared to FL/CS TiO₂ system. A detailed mechanism of sensitized degradation was proposed and a mechanistic model for the rate of degradation of the phenolic compound was derived using the pyramidal network reduction technique. It was found that at low initial dye concentrations, the rate of degradation of the phenolic compound is first order in the concentration of the dye, while at high initial dye concentrations, the rate is first order in the concentration of the phenolic compound. The order of degradation of the different phenolic compounds follows: CP > TCP > DCP > phenol. The different phenolic and dye intermediates that were formed during the degradation were identified by liquid chromatography–mass spectrometry (LC–MS) and the most probable pathway of degradation is proposed.

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1. Introduction

Solar radiation is the most abundantly available renewable and clean source of energy, which is composed of more than 50% of visible radiation and less than 4% of ultraviolet (UV) radiation [1]. In the UV region, pristine TiO₂ has been the “benchmark photocatalyst” for the degradation of organic compounds, reduction of metal ions, and destruction of microorganisms. However, the wide band gap (3.2 eV) of pristine TiO₂ makes it a poor photocatalyst in the solar/visible region. Some of the modifications of TiO₂ to enable its visible light response include, (i) anion doping to narrow the band gap, and (ii) heterostructuring with other narrow band gap semiconductors or dyes as sensitizers [2]. In this report, we focus on coupling an organic dye with TiO₂ to induce the degradation of phenolic compounds in the presence of visible light.

It is well known that singlet oxygen (¹O₂(¹Δ_g)), formed by the interaction of the triplet state of the dye with molecular oxygen, is the key species involved in the sensitized oxidation of organic compounds in the absence of a heterogeneous photocatalyst [3]. However, in the presence of a semiconductor photocatalyst like TiO₂, the mechanism of sensitization is quite different. The mechanism involves the excitation of the dye from the ground state (D) to the triplet excited state (D*) by the action of a visible light photon (λ > 400 nm). This excited state dye species is converted to a

semioxidized radical cation (D^{•+}) by the injection of an electron (e⁻) into the conduction band (CB) of TiO₂ [1]. This trapped electron then forms superoxide radical anion (O₂^{•-}) by the reaction with dissolved oxygen in the system (Fig. 1), which results in the formation of hydroxyl species (OH[•]). These OH[•] radicals are responsible for the oxidation of the organic compounds. Dye sensitized degradation is primarily driven by good adherence of the dye onto the surface of TiO₂, and the presence of O₂ to scavenge the injected electrons from the conduction band of TiO₂ [4].

Zhang et al. [5] have recently studied the aerobic selective oxidation of alcohols in the presence of an anthraquinonic dye (alizarin red S) sensitized TiO₂, and a nitroxyl radical (2,2,6,6-tetramethylpiperidinyloxy). The mechanism involves the formation of a dye radical cation, which oxidizes the nitroxyl radical. This oxidized species was found to be responsible for the selective oxidation of alcohols to aldehydes. Yin et al. [6] have shown that the presence of eosin Y (EY) accelerates the degradation of rhodamine B in the presence of P25. Conjugated polymers like poly(aniline) [7] and poly(thiophene) [8] have also been used as sensitizers of TiO₂ for the degradation of dyes. The role of dissolved oxygen and of active species generated by photo-induced reactions in the photocatalytic degradation of phenol was investigated extensively [9]. Although the above studies have elucidated the mechanism of sensitization in terms of electron injection to facilitate the formation of active species, the kinetics of such processes is still obscure due to the presence of the dye and the organic substrate. Furthermore, it is observed that the sensitizing dye also undergoes oxidation and degrades during the reaction. Therefore, a thorough study of the complex interaction of the dye,

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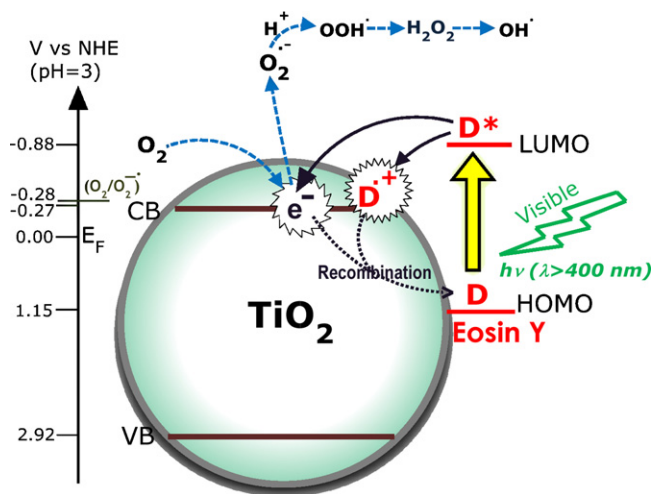


Fig. 1. Mechanism of electron injection from the excited state of EY, and the formation of dye radical cation and superoxide radicals.

organic substrate, and TiO_2 is required to understand the kinetics. In this research work, two xanthene-fluorone dyes, viz., eosin Y (EY) and fluorescein (FL) are employed to sensitize the degradation of substituted phenolic compounds in the presence of combustion synthesized nano- TiO_2 (CS TiO_2). We have shown in our earlier works that CS TiO_2 exhibits higher solar photocatalytic activity compared to the conventional Degussa P-25 TiO_2 (P25) for the degradation of dyes [10].

Cyclic network reduction is a useful method to find the rate of complex reaction networks [11]. Although originally established for homogeneous reactions, the method can also be applied to heterogeneous reactions by assuming pseudo steady state on the intermediate species. Wu and Chern [12] have adopted this technique to derive the rate equation for the photocatalytic degradation of methylene blue. We have also modeled the simultaneous degradation of phenolic compounds and metal ions using dual-cycle network reduction [13], and the sono-photocatalytic degradation of anionic dyes using dual-pathway network reduction techniques [14], respectively. The versatility of this technique has been extended in this work for the dye sensitized degradation of phenolic contaminants. The harmful effects of phenolic contamination in water is well known, as upto 10% of phenol and chlorophenols are widely used as intermediates in the manufacture of chlorinated herbicides and pesticides. Because these organic compounds are toxic, their safe disposal is of primary concern for the environmental remediation.

In the broad scope of waste water remediation, this work is beneficial in two aspects. Firstly, the adsorption of the dye on the

surface of TiO_2 catalyst extends the absorption spectrum of TiO_2 to the visible regime. Secondly, the system containing the dye and the phenolic compound represents a classic model of a real effluent stream, which is usually a mixture of different organic compounds, metal ions and surfactants. Thus, this study assumes importance in the effective detoxification of effluent streams containing a dye and a phenolic compound in presence of visible light source. The kinetic model presented in this work will be useful in the photocatalytic reactor models which utilize dye-sensitized degradation.

Therefore, the purpose of this work is fourfold. Firstly, we have shown the superior activity of CS TiO_2 compared to the commercial catalyst, Degussa P-25 TiO_2 (P25) for the EY sensitized degradation of phenol, 4-chlorophenol (CP), 2,4-dichlorophenol (DCP) and 2,4,6-trichlorophenol (TCP). Secondly, based on the experimental observations, we have proposed a pyramidal network mechanism for the sensitized degradation of the phenolic compounds, and have modeled the reaction using network reduction. Thirdly, we have evaluated the rate coefficients of degradation of the phenolic compounds, and rationalized them based on the mechanism of degradation. Finally, we have suggested a possible pathway of degradation by identifying the phenolic and dye intermediates.

2. Experimental

2.1. Materials

The phenolic compounds, viz., phenol (Rankem Chemicals, India), 4-chlorophenol (CP; S.D. Fine Chem., India), 2,4-dichlorophenol (DCP; Spectrochem, India), 2,4,6-trichlorophenol (TCP; Central Drug House, India) and 4-nitrophenol (NP; Spectrochem, India), and the dyes, viz., eosin Y (EY; Color index (C.I.) No. 45380; Merck, India), fluorescein sodium (FL; C.I. No. 45350; Rolex Laboratories, India) were used as received. The structures of the dyes are presented in Fig. 2. The purity of the above compounds was c.a. 95–99%. Titanium tetra isopropoxide (Alfa Aesar) and glycine (S.D. Fine Chem., India) were used for the synthesis of CS TiO_2 . Potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$), glacial acetic acid, ammonia solution and HPLC grade acetonitrile were obtained from Merck, India. Degussa P-25 TiO_2 was obtained from Degussa Corporation. Water was double distilled and filtered through Millipore (0.45 μm) filter before use.

2.2. Catalyst synthesis and characterization

Solution combustion technique was used to synthesize nano-sized anatase phase TiO_2 . In this method, stoichiometric quantities of aqueous titanyl nitrate (prepared by the hydrolysis and subsequent nitration of titanium tetra isopropoxide) and glycine were combusted at 350 °C in a muffle furnace. A detailed synthesis methodology and the characterization of the catalyst are available

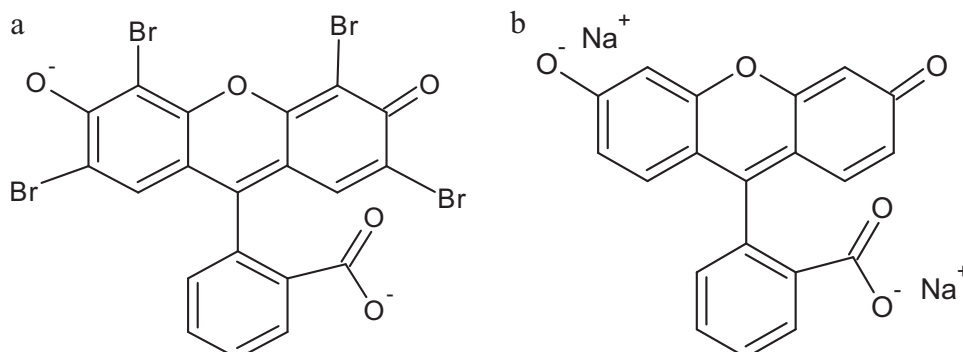


Fig. 2. Molecular structure of (a) eosin Y and (b) fluorescein (sodium salt).

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